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Ultrahigh vacuum ESR studies on clean metal surfaces: NO₂ on copper^{a)}

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(Received 4 April 1980; accepted 1 May 1980)

While ESR has been applied extensively to study surface adsorbates and catalysis,¹ almost no ESR is on clean surfaces prepared under UHV conditions.² We report in this Communication our preliminary results using a new technique for the *in situ* study of molecular adsorption and reactions of gases on metallic surfaces prepared under UHV conditions. Our objectives are to comparatively study both "clean" and "real" metallic and related surfaces. Such studies should relate to the role of surface impurities and defects on the reactivity of metals. They have the added value that studies on real systems can signify those appropriate for more extensive UHV work. In particular, we report on NO₂ adsorbed on various Cu surfaces.

The heart of our design is the UHV-ESR resonant microwave cavity (cylindrical TE011 mode) with high unloaded *Q* (20 000) antenna-coupled to the microwave bridge and an integral part of the UHV system such that vacuum evaporation of clean metal films onto its *interior surface* may be performed. This is accomplished with a tungsten heater element that can be moved through one of the cavity stacks using a bellows drive. We have evaporated Ag and Cu on the inner surface of the ESR cavity under UHV conditions (10⁻⁹-10⁻¹⁰ Torr). The ESR sensitivity of this cavity is $\sim(N_{\text{min}}) \sim 10^{12}$ spins per G, which is close to theoretical for this cavity design and wall loading. Given an effective surface area of the cavity of 50 cm² with perfectly smooth surfaces, or 10-100 times that for thin films produced by vacuum evaporation (which are typically very porous unless annealed), this yields a total of $\sim 10^{18}$ - 10^{19} metal atom surface sites, comparing very favorably with N_{min} .

We summarize our results in order of increasing "cleanliness."

(1) NO₂-Cu/Vycor system: The Cu metal supported on Vycor was prepared in the manner of Clarkson.³ The formation of Cu metal was confirmed by the red-pink color of the sample and no ESR signal due to Cu²⁺. After exposing the sample with 0.1-1 Torr NO₂ at room tem-

perature the sample color immediately changed to blue-gray, and a well-resolved ESR spectrum was observed implying that the Cu on Vycor can be oxidized by NO₂ to form Cu²⁺. The ESR spectrum (Fig. 1A) shows two types of Cu²⁺ complexes with hyperfine and *g*-tensors for which we have a complete analysis.⁴ We tentatively

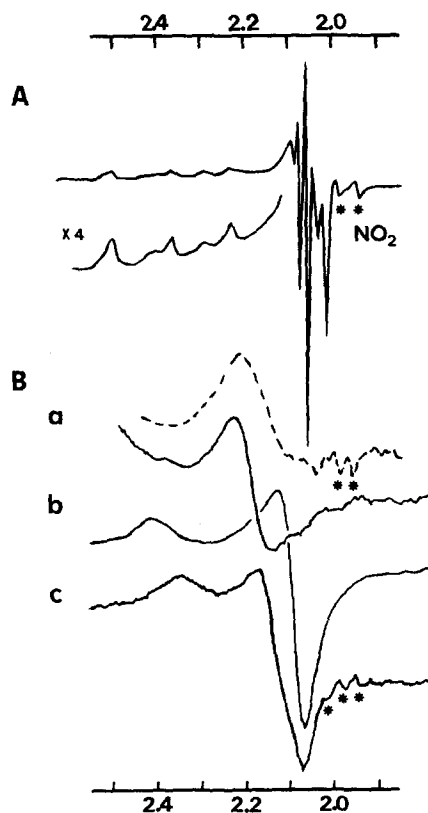


FIG. 1. (A) ESR spectrum from NO₂/Cu/Vycor system showing well-resolved hfs; (B) ESR spectra from NO₂/Cu wire (—) of types a, b, and c (cf. text) and from UHV prepared Cu films + NO₂ (---). *x*-axis gives *g*-values; * shows NO₂ lines.

assign them to a distorted octahedral structure (formed from initially unreduced Cu^{2+}) and to a distorted square planar structure (formed from Cu^0).⁴ The well resolved Cu hfs indicates that these complexes consist of well-isolated Cu^{2+} ions on the Vycor surface.

(2) Cu wire: 99.999% pure Cu wire was precleaned by successive baking in H_2 , O_2 , then H_2 . Small (several mg) samples could be introduced into the standard cavity in sample holders under vacuum ($\sim 10^{-6}$ Torr) without seriously affecting cavity Q . Properly cleaned samples show no ESR signals from Cu^{2+} . When NO_2 is admitted at 77°K ESR spectra of gas-phase molecular oxygen can be observed possibly from NO_2 decomposition. The reaction with Cu starts when NO_2 condenses at -30°C and 5 Torr yielding species (a). Three types of ESR spectra (Fig. 1B) are observed: (a) symmetric singlet ($g = 2.19$, $\Delta H_{pp} = 100$ G); (b) asymmetric signal ($g_{\parallel} = 2.41$, $g_{\perp} = 2.09$); (c) asymmetric signal ($g_{\parallel} = 2.34$, $g_{\perp} = 2.11$). No hfs can be resolved. Normally an irreversible process occurs easily from species (a) to (c), and isolation of (b) requires the process to be frozen at lower temperature immediately after the formation of (a). Species (c), the final product of oxidation, could be the same as (or similar to) the first species seen on Cu/Vycor. The important spectral difference that hfs is seen for Cu/Vycor but not on Cu metal is attributed to the fact that, on the pure metal, adjacent sites become paramagnetic, so they can exchange-narrow the hfs, while on Cu/Vycor one only sees spectra from separated Cu^{2+} ions with negligible exchange interactions. The fact that the anisotropy in g -tensor is *not* averaged out on the pure metal is taken to imply that the Cu^{2+} ions are microscopically crystalline.⁵ (Cu wire experiments have also been performed in the UHV system.)

(3) Experiments have been performed on evaporated Cu films on the inner surface of the UHV cavity with vacua of 10^{-9} – 10^{-10} Torr after bakeout. Vacuum deposition of 99.999% Cu wire onto a Cu base for 10 min resulted in a mean thickness of film of 100–200 Å. Best experimental results are obtained by introducing NO_2 into the UHV system close to the ESR cavity rather than downstream nearer the UHV pumps, ion gauge, and mass analyzer. There is no evidence of O_2 formation with introduction of NO_2 . (Our UHV-ESR cavity is particularly sensitive to the presence of paramagnetic gases which can fill the whole cavity.) A very high dosage of NO_2 (viz. flowing NO_2 at 10 mTorr for 1 min at -100°C) is required before the reaction can be induced to occur, yielding a broad nearly symmetric ESR signal of over

100 G which is very similar to Spectrum a (Fig. 1), but no Spectrum c is found. Current experiments with O_2 and/or H_2O predosing and O_2/NO_2 mixtures indicate, consistent with the above, that O_2 and/or H_2O may play an effective role in causing Spectrum c to form.

These results indicate differences in properties of Cu/Vycor, Cu metal, and clean Cu films as well as differences between conventional and UHV preparations. Our UHV-ESR technique should be applicable to other metal films and to the preparation and study of "clean" oxide surfaces as well as "supported metal" surfaces.

Another intriguing feature of the UHV experiments is the observation of an intense $g = 2$ and narrow ($\Delta H \approx 10$ G) electron-cyclotron resonance at pressures less than 10^{-2} Torr. We propose that stray electrons can absorb enough microwave energy to knock additional electrons off the cavity walls to start an electron avalanche. This cyclotron resonance is quenched by the residual gas above 10^{-2} Torr and by microwave powers below a threshold value ($P_i \sim 1$ – 10 mW incident) needed to sustain a steady-state emission. We can use P_i to indicate how clean and free from defects is the Cu film. Fresh Cu films exhibit the highest $P_i \sim 10$ mW, while films heavily dosed with NO_2 exhibit very low $P_i \sim 1$ mW. Also P_i can be increased by biasing the electrically isolated endplate of the cavity.

We are indebted to Professor R. P. Merrill, Professor T. N. Rhodin, and Professor J. M. Blakely for their extensive help and advice on UHV techniques.

⁴Supported by Grant No. ER-78-C-02-499-A000 from the Office of Basic Energy Sciences of the DOE, by the Cornell Materials Science Center (NSF), and acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the ACS, for partial support (Grant No. 10935-N5).

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